

5

### Catalytic composition of organotin compounds

The present invention relates to catalytic compositions for esterification, transesterification and polycondensation reactions, a process for the  
10 catalysis of said reactions employing such catalytic compositions and polyesters or resins obtainable by this process.

Catalytic systems containing organotin compounds are widely known.

15 E.g. compounds of the formula  $[(RSn)_{12}O_{14}(OH)_6]^{2+}$  are described mainly in connection with their interesting structure in: H. Puff, H. Reuter, J. Organomet. Chem. 1989, 373, 173-184; D. Dakternieks, H. Zhu, E. R. T. Tiekink, R. Colton, J. Organomet. Chem. 1994, 476, 33-40; S. Durand, K. Sakamoto, T. Fukuyama, A. Orita, J. Otera, A. Duthie,  
20 D. Dakternieks, M. Schulte, K. Jurkschat, Organometallics 2000, 19, 3220-3223.

Compounds of said type  $[(RSn)_{12}O_{14}(OH)_6]^{2+}$  are further described to show a poor performance in catalyzing or activating reagents and  
25 compounds within the acetylation reaction of acetic anhydride with an alcohol (S. Durand, K. Sakamoto, T. Fukuyama, A. Orita, J. Otera, A. Duthie, D. Dakternieks, M. Schulte, K. Jurkschat, Organometallics 2000, 19, 3220-3223.)

30

- 2 -

It is known for compounds of the formula  $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$  when stored in methanol, that a replacement of two structural important  $\mu_2$ -bridged OH groups of the cluster against  $\text{OCH}_3$  units can occur (D. Dakternieks, H. Zhu, E. R. T. Tiekink, R. Colton, , J. Organomet. Chem. 1994, 476, 33-40).

Furthermore is known that during the production of polyesters for some applications for example wrappings and technical yarns, a crystallization and polycondensation in the solid state is carried out (US-A-4,064,112, US-A-4,263,425, US-A-5,362,844). In other applications, fibers or filaments are spun directly and direct preforms are produced in a process wherein an intermediate transfer into the solid state and a repeated remelting is not applied.

Conventional polyester compositions are connected with a series of disadvantages (general summary in: Handbook of polyester thermoplastics, 1st edition, Wiley-VCH, Weinheim, 2002). Among these disadvantages are in particular:

- Necessity of high temperatures for the synthesis
- High catalyst concentration (100-500 ppm [as metal])
- Degradation processes under processing and polycondensation conditions; for example formation of vinyl esters and due to the formation of acetic aldehyde in polyethylene terephthalate (PET), formation of acrolein in polypropylene terephthalate (PPT) and tetrahydrofuran formation in polybutylene terephthalate (PBT).
- Limited use of the catalyst systems, dependent on the technology of the process and the chemical structure of the substrate; classic titanium based catalysts cannot be added for example during the esterification- and/or pre/condensation step, as these are readily hydrolyzed to inactivate titanium oxides.

- 3 -

- Application of the catalyst system only in selected process stages for example only during the esterifications- or only during the transesterification- or only during the polycondensation stage.

- Optical turbidity of the produced polyester for example by deposits of elementary metal impurities as this can occur by the use of antimony based catalyst systems.

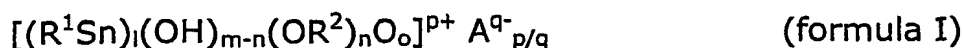
- Discoloration of the polyester by the catalyst itself, for example titanium based catalyst systems cause a yellow coloring of the polymer or formation of chromophor by-products, respectively.

- Problematic metering and addition of catalysts and catalyst formulations.

Object of the present invention is to provide a catalytic composition, suitable for catalyzing esterification, transesterification and polycondensation reactions, an improved process of catalyzed esterification, transesterification and polycondensation reactions and the production of improved polyesters for bottles, films, foils, yarn, molded padding, resins for powder coatings and technical synthetic materials, which avoid the disadvantages of the prior art.

The problem is solved according to the invention by a catalytic composition according to claim 1, a process for the preparation of such catalytic compositions according to claim 7, their use according to claim 10 and polyesters or resins according to claims 18 and 19.

A first embodiment of the present invention refers to a catalytic composition for esterification, transesterification and polycondensation reactions of dicarboxylic acids, polycarboxylic acids, hydroxy carboxylic acids and/or their derivatives and alcohols containing at least one tin compound of the general formula (I):



wherein:

- 5  $R^1$  and  $R^2$  each independently is a linear, branched or cyclic alkyl group or aryl group having 1 to 12 carbon atoms,  
 $A^{q-}$  is an anion,  
 $l$  is at least 1,  
 $m = 0$  to 20,  
10  $n = 0$  to 20,  
 $p = 0$  to 6,  
 $o = 0$  to 20 and  
 $q = 0$  to 6.
- 15 Preferred examples for  $R^1$  are methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo pentyl radical, tert-pentyl, hexyl, heptyl, n-octyl, iso-octyl, 2-ethyl-1-hexyl, 2,2,4-trimethylpentyl, nonyl, decyl, dodecyl, n-dodecyl, cyclopentyl, cyclohexyl, cycloheptyl, methylcyclohexyl, vinyl, 1-propenyl, 2-propenyl,  
20 naphthyl, anthranyl, phenanthryl, o-tolyl, p-tolyl, m-tolyl, xylyl, ethyl phenyl, mesityl, phenyl, benzyl. Favored substituents for the invention are: Methyl, n-butyl, n-octyl and n-dodecyl.

- Examples for  $R^2$  are methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-butyl,  
25 iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo pentyl, tert-pentyl, hexyl, heptyl, n-octyl, iso-octyl, 2,2,4-trimethylpentyl, 2-hydroxy-1-ethylpentyl, hydroxy-neo-pentyl, 2-ethyl-1-hexyl, nonyl, decyl, dodecyl, n-dodecyl, cyclopentyl, cyclohexyl, cycloheptyl, methylcyclohexyl, vinyl, 1-propenyl, 2-propenyl, naphthyl, anthryl, phenanthryl, o-tolyl, p-tolyl,  
30 m-tolyl, xylyl, ethyl phenyl, mesityl, phenyl, benzyl. Favored

- 5 -

substituents for the invention are: Methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-butyl, iso-butyl, tert-butyl.

Preferred examples for A are: O, OH, methanolate, ethanolate, n-  
5 propanolate, iso-propanolate, n-butanolate, 2-butanolate, iso-  
butanolate, tert-butanolate, n-pentanolate, iso-pentanolate, neo-  
pentanolate, tert-pentanolate, 2-methyl-1-butanolate, hexanolate,  
heptanolate, n-octanolate, iso-octanolate, 2,2,4-trimethylpentanolate,  
nonanolate, decanolate, dodecanolate, n-dodecanolate,  
10 cyclopentanolate, cyclohexanolate, cycloheptanolate,  
methylcyclohexanolate, glycolate, glycerate, pinakolate  
neopentylglycolate, vinylalkoholate, propargylalkoholate, 2-ethyl-1-  
hexanolate, formiate, acetate, propionate, butyrate, valerate, caprate,  
caprylate, caprinate, laurate, laureate, 2-ethyl-1-hexanoate,  
15 neodecanoate, palmitate, stearate, benzoate, terephthalate, phthalate,  
isoterephthalate, acrylate, methacrylate, crotonate, isocrotonate,  
vinylacetate, oleate, sorbate, linolate, linolenate, trifluoroacetate,  
methansulphonate, ethanesulphonate, n-propanesulphonate, iso-  
propanesulphonate, n-butanesulphonate, 2-butanesulphonate, iso-  
20 butanesulphonate, tert-butanesulphonate, n-pentanesulphonate, iso-  
pentanesulphonate, neo-pentanesulphonate, tert-pentanesulphonate, 2-  
methyl-1-butanesulphonate, hexanesulphonate, heptanesulphonate, n-  
octanesulphonate, iso-octanesulphonate, 2,2,4-trimethylpentan  
sulphonate, nonansulphonate, decansulphonate, dodecanesulphonate,  
25 n-dodecanesulphonate, cyclopentanesulphonate, cyclohexane  
sulphonate, cycloheptanesulphonate, methylcyclohexanesulphonate p-  
toluolsulphonate, oxalate, malonate, succinate, glutarate, adipate,  
fumarate, maleinate, carboxylates of the following monoesters:  
methylmaleic acid monoester, ethylmaleic acid monoester, butylmaleic  
30 acid monoester, n-propylmaleic acid monoester, iso-propylmaleic acid

monoester, n-butylmaleic acid monoester, 2-butylmaleic acid monoester, iso-butylmaleic acid monoester, tert-butylmaleic acid monoester, n-pentylmaleic acid monoester, isopentylmaleic acid monoester, neo-pentylmaleic acid monoester, tert-pentylmaleic acid monoester, 2-methyl-1-butylmaleic acid monoester, hexylmaleic acid monoester, heptylmaleic acid monoester, n-octylmaleic acid monoester, iso-octylmaleic acid monoester, 2,2,4-trimethylpentylmaleic acid monoester, nonylmaleic acid monoester, decylmaleic acid monoester, dodecylmaleic acid monoester, n-dodecylmaleic acid monoester, cyclopentylmaleic acid monoester, cyclohexylmaleic acid monoester, cycloheptylmaleic acid monoester, methylcyclohexylmaleic acid monoester, glycolmaleic acid monoester, glycerolmaleic acid monoester, pinakolmaleic acid monoester, neopentylglycolmaleic acid monoester, vinylmaleic acid monoester, propargylmaleic acid monoester and 2-ethyl-1-hexylmaleic acid monoester, citrate, lactate, tartrate, naphthenate, naphthalene-2,6-dicarboxalate, naphthalene-1,6-dicarboxalate, F, Cl, ClO, ClO<sub>2</sub>, ClO<sub>3</sub>, ClO<sub>4</sub>, CO<sub>3</sub>, Br, J, CN, SCN, OCN, sulphate, hydrogensulphate, sulphite, hydrogensulphite, sulphide, phosphate, hydrogenphosphate, dihydrogenphosphate, bis(2-ethyl-1-hexyl)phosphate, butylphosphate, dibutylphosphate, 3-phosphonopropionate, phenylphosphoic acid, benzylphosphoic acid, p-aminophosphoic acid, n-octylphosphoic acid. Favored substituents for the invention are: methanolate, ethanolate, n-propanolate, isopropanolate, n-butanolate, 2-butanolate, iso-butanolate, tert-butanolate, bis(2-ethyl-1-hexyl)phosphate, neodecanoat, 2-ethylhexanoat, and 2-ethyl-1-hexylmaleic acid monoester, trifluoroacetate, p-toluolsulphonate, Cl, Br, J, sulphate, hydrogen sulphate, phosphate, hydrogen phosphate and dihydrogen phosphate.

- 7 -

Said catalytic compositions proved highly effective in the catalysis of esterification, transesterification, polycondensation, polyesterification and polytransesterification reactions. These derivatives of dicarboxylic acids, polycarboxylic acids and/or hydroxy carboxylic acids according to the invention include e.g. esters and halogenides, but not anhydrides.

In a preferred embodiment of the invention, said catalytic composition is characterized in that the anion  $A^{q-}$  is  $O^{2-}$ ,  $-OH^-$ , a linear, branched or cyclic alkyl carboxy or aryl carboxy group or linear, branched or cyclic alkoxy group each having 1 to 12 carbon atoms, the anion of a mineral acid or a metalate.

In particular, said anion  $A^{q-}$  is a sulphate, sulphite, phosphate, halogenide or pseudo-halogenide, titanate, zirconate, aluminate or zincate anion.

According to a particularly preferred embodiment of the invention, said catalytic composition is characterized in that  $n = 1$  to 20.

In this case a specific structure within the  $[(R^1Sn)_l(OH)_{m-n}(OR^2)_nO_o]^p + A^{q-}_{p/q}$ -unit is created by introduction of 1 to 20 alkoxy groups ( $OR^2$ ).

Most preferred catalytic compositions according to the invention are characterized in that  $l = 12$ ,  $m = 6$ ,  $n = 0$  to 6,  $o = 14$  and  $p = 2$ .

Since the chemical composition containing a tin compound according to formula I, having  $R^1 = \text{butyl}$ ,  $R^2 = \text{methyl}$ ,  $l = 12$ ,  $m = 6$ ,  $n = 2$ ,  $o = 14$ ,  $p = 2$ ,  $A = Cl$ ,  $q = 1$ , as such is known but is described to be used for different purposes than that of the present invention, the catalytic

composition according to the present invention does not encompass the protection of said species as such.

According to the invention the specific structure within  
5  $[(R^1Sn)_l(OH)_{m-n}(OR^2)_nO_o]^{p+} A^{q-}_{p/q}$  -unit is achieved by introduction of 1 to 20, preferably 1 to 6 alkoxy groups ( $OR^2$ ) into the unit  $[(R^1Sn)_l(OH)_mO_o]^{p+} A^{q-}_{p/q}$  - by conversion with suitable metal alkoxides (metal alcoholates).

10 Preferred examples for said metal alkoxides are: Li, Na, K, Rb, Mg, Ca, Sr, Ba, Sc, Ti, Zr, Hf, Zn or Al-methanolate -ethanolate, -n-propanolate, -iso-propanolate, -n-butanolate, -2-butanolate, -iso-butanolate, -tert-butanolate, -neo-pentanolate, -isopentanolate, -neo-pentanolate, -tert-pentanolate, -2-methyl-1-butanolate, -hexanolate, -heptanolate, -n-  
15 octanolate, -iso-octanolate, -2, 2, 4-trimethylpentanolate, -nonanolate, -decanolate, -dodecanolate, -n-dodecanolate, -cyclopentanolate, -cyclohexanolate, -cycloheptanolate, -methylcyclohexanolate, -glycolate, -glycerate, -pinakolate, -neopentylglycolate, -vinylalcoholate, -propargylalcoholate, -2-ethyl-1-hexanolate. Favored metal alcoholates  
20 are: Sodium methanolate, potassium t-butylate, aluminium methanolate -ethanolate, -n-propanolate, -iso-propanolate, -n-butanolate, -2-butanolate, -iso-butanolate, -tert-butanolate, -neo-pentanolate and -iso-pentanolate, titan tetra-butanolate.

25 According to the invention the conversion of the units  $[(R^1Sn)_l(OH)_mO_o]^{p+} A^{q-}_{p/q}$  with a metal alkoxide is preferably carried out using said metal alkoxide in a proportion of 1:0.0001 up to 1:20 by mole, in particular 1 : 4 to 1 : 6 .



- 9 -

It is furthermore preferred that the side products resulting from said conversion of the metal alkoxides with  $[(R^1Sn)_l(OH)_mO_o]^{p+} A^{q-}_{p/q}$  -units remain in the reaction mixture. These side products include e.g. metallic oxides, metal hydroxides and alkoxy metal hydroxides further to the catalytically active compounds  $[(R^1Sn)_l(OH)_{m-n}(OR^2)_nO_o]^{p+} A^{q-}_{p/q}$ . The side products of the metal alkoxides do not affect the activity of the desired compounds  $[(R^1Sn)_l(OH)_{m-n}(OR^2)_nO_o]^{p+} A^{q-}_{p/q}$ .

In a further embodiment of the invention, the catalytic composition as defined above is used for the continuous or batchwise production of esters or polycondensation products by esterification, transesterification, polyesterification or polytransesterification reaction.

Esterification, transesterification, polycondensation, polyesterification and polytransesterification reactions are catalyzed and accelerated by the catalytic compositions according to the invention. The inventors have shown that in comparison to conventional methods lesser amounts of catalyst and lesser amounts of stabilizer lead to comparable results. In addition, even high-viscous polyesters may be produced in a direct process in by far shorter reaction times. The novel catalytic composition of the invention is further resistant to hydrolysis and may be added already during the esterification phase and the precondensation phase or later as an active component.

Preferably, the catalytic composition according to the invention may be used for a polyesterification reaction of a dicarboxylic acid derivative with a mono, divalent or polyvalent alcohol.

It is particularly preferred to employ derivatives of di, or polycarboxylic acids being selected from the group of esters or halogenides.

Dicarboxylic acids (carboxylic acids, containing at least two carboxyl groups), e.g. terephthalic acid, 2,6-naphthalene dicarboxylic acid, isophthalic acid, 1,4-cyclohexanedicarboxylic acid, 1,6-naphthalene dicarboxylic acid, 4,4-bisphenyl dicarboxylic acids, adipic acid, phthalic acid, alkane dicarboxylic acids, halogen derivatives of the mentioned dicarboxylic acids for example tetrabromophthalic acid, and copolymers of the mentioned dicarboxylic acids or the esters of the mentioned carboxylic acids for example dimethyl terephthalate, bis(hydroxyethyl)terephthalate, 2,6-dimethylnaphthalate, 1,6-dimethylnaphthalate and others are preferred according to the invention.

Polyvalent alcohols, such as ethylene glycol, 1,3-propane diol, 1,4-butane diol and/or 1,4-cyclohexane dimethanol, di-, triethylene glycol, polyglycols with a molecular weight below 1000 or neopentyl glycol, are preferably employed.

The catalytic compositions of the invention may further advantageously be used for the production of polyesters from hydroxycarboxylic acids such as p-hydroxybenzoic acid, salicylic acid, lactic acid, glycol acid and their co-polyesters with the dicarboxylic acids and/or diols described above.

It is also preferred to employ derivatives of hydroxycarboxylic acids being preferentially selected from esters.

Further recycled polyester material might be used as co/monomer within the scope of the invention.

- 11 -

The metal concentration of the catalytically effective metal compound is preferably 0.1 ppm to 1 mole-%, in particular 10 ppm to 100 ppm, most preferred 20 to 50 ppm with reference to the acid or derivative to be reacted.

5

The catalytic composition used for the production of polyester may be added during the period before the beginning of the esterification and/or transesterification until shortly before the end of the polycondensation, favored during the esterification and/or transesterification or before the  
10      precondensation steps of the production process.

15

A solvent or suspending agent can be added to the tin compound prior or during the manufacturing of the catalytic composition and/or said esterification, transesterification, polyesterification or polytransesteri-  
15      fication reaction.

20

As solvents or suspending agents for the catalyst an alcohol and/or an alkane diol can be employed, favored are 1,2-ethane diol, 1,3-propane diol, 1,4-butane diol, 2,2-dimethylpropane-1,3-diol.

25

The solvent or suspending agent used according to the invention may be different or the same in the manufacturing of said catalytic composition and said esterification, transesterification, polyesterification or polytransesterification reaction.

30

A preferred solvent or suspending agent employed in the invention is being selected from the group of mono-, di- or polyvalent alcohols being reacted in said esterification, transesterification, polyesterification or polytransesterification reaction.

- 12 -

Further preferred solvent or suspending agents include an organic liquid that is indifferent with respect to the polyester production process. Examples for such indifferent organic liquids are alkanes, cycloalkanes or benzene derivatives such as benzene, toluene or xylenes. Moreover,  
5 water or a mixture of water with an alcohol or a polyvalent may be employed as solvent and/or suspending agent.

Further additives for a color correction such as cobalt salts or organic dyes or pigments may be added to the reaction mixture, preferably in  
10 amounts of 0.0001-5% by weight, in relation to the acid or derivative to be reacted.

The polyester available by the process using the catalytic compositions of the invention shows at least comparable qualities with respect to  
15 processibility as traditional polyesters, e.g. catalyzed with antimony. In comparison to conventional high-viscosity melt polymerisations, resins produced using the catalytic compositions described by the invention show a relatively low content of acetic aldehyde. In particular the polyesters synthesized with the process described by the invention show  
20 a narrow molecular weight distribution, a high translucency and give a polymer with a high, desired blue shift. A polymer of high viscosities, unlike the state of the art using Sb catalysts, obtained without difficulty.

The polymers, produced using catalytic compositions of the invention  
25 show a high blue shift (negative b-values; color values determined by using the CIE-Lab 100 color system with spectral reference beam color measuring instrument LUCI 100, Dr. Lange).

The polyesters manufactured by a process using the catalytic  
30 compositions of the invention are made by esterification and, optionally,

- 13 -

subsequent polycondensation. These polyesters are especially suited for bottles, films, foils, yarn and/or molded padding, or resins for powder coatings or technical synthetic materials,

- 5 Preferred polyesters according to the invention include:
- a) polyethylene terephthalate (PET), containing 0.1-10 mass % diethylene glycol and 0-10 mass % of isophthalic acid, 2-hydroxy-isophthalic acid, p-hydroxyisophthalic acid, 2,6-naphthalenedicarboxylic acid and/or 1,4-cyclohexane dimethanol as co-monomer;
  - 10 b) polyester for powder coatings mainly poly-2,2-dimethylpropyl-1,3-terephthalate;
  - c) polypropylene terephthalate (PPT);
  - d) polyester polyols as for example polydiethyleneglycol terephthalate;
  - e) polybutylene terephthalates (PBT);
  - 15 f) polynaphthalene terephthalates (PNT)
  - g) polyethylene naphthalate (PEN).

The following examples illustrate the invention further without, however, limiting the invention. Unless otherwise indicated, parts and  
20 percentages relate to the weight, as in the remainder of the description.

Further subjects of the invention are described by the claims and are in total part of the description of the present invention.

25

30

**Examples:**Example 1: List of catalytically acting tin-containing compositions:5    **Apparatus:**

250 ml three necked round bottom flask, tap funnel, magnetic stirrer, water separator, rotary evaporator.

10   **Starting materials, quantities:**

monobutyltin oxide	20,88 g	[0,10 mol]
bis(2-ethylhexyl) phosphate	5,15 g	[0,016 mol]

15   **1a) without alcoholate**

1b) titanium tetrabutanolate                      4,25 g                      [0,0125 mol]

1c) sodium methanolate                              2,70 g                      [0,05 mol]

1d) aluminum triethoxide                            2,60 g                      [0,016 mol]

1e) aluminum tri(sec-butoxide)                    4,40 g                      [0,016 mol]

20   

1f) aluminum tri(isopropoxide)                    3,39 g                      [0,016 mol]

**Synthesis:**

Monobutyltin oxide was suspended in xylene (150 ml), bis(2-ethylhexyl)phosphate was added within 10 min and the suspension is heated under reflux until the water formation stopped. After reaching room temperature the reaction was filtered. The metal alcoholate was added to the filtrate, which was then heated under reflux for an additional hour. The product was received after removal of the solvent under reduced pressure.

25  
30

Further alkyltin catalysts:

Comparative Example 1g (Tributyltin (2-ethylhexanoate):

5

A three-necked flask equipped with mechanical mixer, heating, thermometer and vacuum distillation bridge was, under nitrogen protective atmosphere, filled with 149 g (0,25 Mol) hexabutyldistannoxane and 72,1 g (0,5 Mol) 2-ethylhexanoic acid. The reaction mixture was heated up on 80°C. To separate from the reaction water a vacuum of 1 mbar was applied, and the reaction mixture was stirred another 1 h at this temperature.

10

Yield: 209,8 g (theoretical. 212,1 g) a clear, bright liquid.

Elemental analysis: Sn content = 27,8 %.

15

The production of the examples and comparative examples 1h to 1n followed the same procedure.

Comparative example 1h: Dibutyltin bis(2-ethylhexanoate)

20

Example 1i: monobutyltin tris(2-ethylhexanoate)

Comparative example 1j: dibutyltin pinacolate

25 Example 1k: monooctylstannoic acid

Example 1l: monobutylstannoic acid

Example 1m: monooctyltin tris(2-ethylhexanoate)

30

Example 1n: monododecyltin tris(2-ethylhexanoate)

Example 2: Catalyst test by synthesis of a resin for powder coatings:

5 Starting materials, quantities:

terephthalic acid                      83,07 g                      [0,50 mol]

neopentyl glycol                      (2,2-dimethyl-1,3-propandiol)

10    104,15 g                      [1,00 mol]

catalyst:                                      0,05 % [m/m] (as metal)

Synthesis:

15

Catalyst, neopentyl glycol and terephthalic acid were given into a 250 ml three necked round bottom flask. The mixture was heated to a maximum by the means of a heating mantel and the reaction water was distilled off and the amount was measured.

20

The reaction time equals the time between the first water formation and the „clear point“ of the reaction.

25

Table 1 shows the acceleration of the reaction time in the described resin synthesis with the mixtures of examples 1a, 1b, 1c, 1d, 1e, 1f in comparison with the uncatalized reaction or with monobutyltin oxide (0,05 % [m/m]) as catalyst.

30



Table 1: Reaction time of the mixtures a-f in comparison.

Catalyst (0,05% as Sn)	Volume H <sub>2</sub> O [ml]:												[min]	Remarks
	15 min	30 min	45 min	60 min	75 min	90 min	105 min	120 min	135 min	150 min	165 min	180 min	Reac- tion time	
Without catalyst				1		1		2		3		4	300	aborted
monobutyl- tin oxide		7		9		12		15		17		19	180	Clear, colorless
1a		7		10		18							90	Clear, colorless
1b	3	6	5	9	11	14							90	hazy, colorless
1c	4	4	10	14	16								75	Clear, colorless
1d	3	6	10	12	14	16							90	Clear, colorless
e	3	5	6	8	9	10	13	15	18				135	Clear, colorless
f	3	5	7	10	12	14	15	16	18				135	Clear, colorless

5 Example 3: Catalytically active Sn-compounds with A = alcoholate:

Example 3o: Product of the reaction of monobutyl stannic acid with Ti(OBu)<sub>4</sub> (molar ratio 4 : 1):

- 10 51,1 g (0,15 mol) Ti(OBu)<sub>4</sub> and 25.3 g (0,60 mol) monobutyl stannic acid were dissolved in xylene (250 ml) and refluxed under a nitrogen atmosphere in a 500 ml three necked round bottom flask for 4 hours. The product was obtained after the solvent was removed under reduced pressure in an amount of 149,6 g (theoretical. 131,9 g) as a yellow
- 15 solid (Elemental analysis: Sn content = 46,5 %, Ti content = 4,9 %).

Example 3p: Product of the reaction of monooctyl stannic acid with  $\text{Ti}(\text{O}i\text{Bu})_4$  (molar ratio 1 : 1), synthesis in analogy to catalyst o.

- 5 Example 3q: Product from monooctylstannoic acid with tetrabutyl titanate (amount of substance ratio 4: 1), synthesis in analogy to Example 3o.

- 10 Example 3r: Product from monobutylstannoic acid with tetrabutyl titanate (molar ratio 2 : 1), synthesis in analogy to Example 3o.

Example 4: Polycondensation of bis(2-hydroxyethyl) terephthalate (BHET):

15 Experimental method

Polycondensation equipment 1 (glass equipment) for the melt polycondensation of BHET

- 20 Tempering-bath (salt bath), polycondensation vessel (glass), screw mixer (glass), vacuum pump, pressure gauge

- As a polycondensation equipment a round glass flask with round bottom was used, (internal diameter 2,6 cm, and 35 cm height, described in T. Johnson, Chem. Fibers International 46 (1996) 280; 49 (1999) 455). A horizontal vapor outlet is integrated into the upper third of the flask wall. A further extension tube near the bottom of the vessel allowed sampling from the polymer melt. The stirrer was a glassware screw mixer, reaching down to the ground (1,8 cm diameters). The mixer was
- 25

- 19 -

operated with a rotation speed of  $100 \text{ min}^{-1}$  and intermixed the melt with axially downward direction.

25,4 g (0,1 mol) BHET were filled into the polycondensation vessel, the catalyst (5 to 200 ppm as metal) was added and the vessel locked. Then the polycondensation vessel filled with the reaction mixture was evacuated three times and flushed with dry nitrogen before it was immersed in the tempering-bath. The bath temperature was preset so that the desired internal temperature of  $280^{\circ}\text{C}$  was reached in the polycondensation vessel. After the reaction mixture was melted, the stirrer was started and the vessel evacuated within 15 min onto a vacuum of  $2 \times 10^{-1}$  mbar. The time of the first formation of glycol at the wall of the glass was regarded as  $t_0$ . The attainable final pressure for this equipment of approximately 4 to  $5 \times 10^{-2}$  mbar, was reached after approx. 1 h experimental time, depending on the progress of the polycondensation. Through the sampling device samples could be taken by means of a VA steel wire, maintaining a nitrogen counter flow. At the end of the reaction up to 5 g could be taken from the vessel for further analysis. During the polycondensation, an average sampling required one minute, from breaking the vacuum to re-applying the vacuum. At the end of the polycondensation sampling was done within two minutes after aerating the vacuum.

## PET characterization

The determination of the intrinsic viscosities was performed as follows:

The relative solution viscosities  $\eta_{\text{rel}}$  for PET were determined in phenol (3 parts) / dichlorobenzene (2 parts) mixtures using 0.5 percent

- 20 -

solutions at 25 °C. The conversion of the relative solution viscosities into the intrinsic viscosity  $[\eta]$  was done according to BILLMEIER.

$$\eta_{\text{intr}} = \frac{1}{4} \frac{\eta_{\text{rel}} - 1}{c + \frac{3}{4}} \times \frac{\ln \eta_{\text{rel}}}{c}$$

From the intrinsic viscosities (IV) the average molecular weights  $M_n$  (number average) as well as the degrees of polymerization  $P_n$  were calculated. For PET applies:  $M_n = (1000 \times IV)^{1,5186}$ ;  $P_n = M_n/192$ .

The absolute viscosities were measured using the viscosimeter AVS 250 and the tempering-unit CT 1450 of Schott Geräte GmbH, Germany. Comparison measurements between different laboratories gave matching results.

The color values were determined using the CIE-LAB-Farbsystem (color system) by the spectral reference beam color measuring instrument LUCI 100, Dr. Lange.

The device STA 625 of Polymer Laboratories was used for TG and DSC-measurements.

The COOH end groups were determined by potentiometric titration of the in cresol solution of the polymers with diluted aqueous NaOH.

BHET and the catalyst were introduced into the reaction vessel and rinsed well with nitrogen.

- 21 -

The reaction vessel was placed into the salt bath. Recording of reaction time started now. Within 15 min the pressure was lowered from 100 mbar to 0,09 mbar. At the end of the reaction a pressure of 0,04 mbar was reached.

5

The following table 2 shows the results of the polycondensation experiments for the catalysts of examples 1a, 3p and 3q in comparison to Sb- and Ti-based catalysts (table 3). Criteria for determining catalyst activity are the attainable molecular masses in specific time periods, the increasing influence of the thermal degradation, recognizable by the flattening of the  $P_n$ -t-function as well as the color values of the polyester. The amount of the evolved ethanal (acetaldehyde) that directly correlates with the degree of thermal ester group cleavage is a further essential criterion of the catalyst suitability. The color values in the tables show the discoloration of the product, the a-values representing green/red-gradients and the b-values representing blue/yellow-gradients. Negative a-values correspond to green, negative b-values correspond to blue gradients. Blue shift is favored technologically.

10  
15  
20

The comparative investigations for the catalytic activity of the selected tin compounds show that no noteworthy thermal decomposition is to be expected within 2 h of polycondensation time at temperatures of 280 °C. Therefore it is absolutely possible to synthesize even higher molecular weight polyethylene terephthalates by prolongation of the polycondensation time.

25

All examined tin compounds proved to be high-activity catalysts for the polycondensation of BHET which showed significantly higher activity than stibious compounds. Their polytransesterification activity was

30

superior to that of titanium alkoxides and titanium chelates. If required, they may alternatively be employed in higher concentrations.

Table 2. Polycondensation of BHET with the catalysts of examples 1a,  
5 3p and 3q .

catalyst of example	time [min]	molar ratio Ti/Sn	concentration Sn/Ti [ppm]	M <sub>n</sub> [g/mol]	P <sub>n</sub>	color values using the CIE-LAB-system		
						L	a	b
1a	30	0/1	116	2090	9	-	-	-
1a	60	0/1	116	3812	20	-	-	-
1a	90	0/1	116	6145	32	33.01	-0.05	1.18
1a	120	0/1	116	16559	86	37.81	-0.46	2.64
3p	20	1:1	20/9	3839	20			
3p	42	1:1	20/9	15454	80	67.15	-0.21	1.30
3p	96	1:1	20/9	25733	134	72.79	-1.03	0.61
3p	120	1:1	20/9	28454	148	68.06	-1.06	2.76
3q	15	1:4	20/2.25	1635	8			
3q	31	1:4	20/2.25	4734	24	86.69	-0.87	-4.38
3q	60	1:4	20/2.25	13499	70	70.38	-0.38	-0.31
3q	90	1:4	20/2.25	18759	97	73.54	-0.60	1.43

Table 3. Polycondensation of BHET with Sb and Ti catalysts.

catalyst	temperature [°C]	time [min]	catalyst conc. [ppm]	P <sub>n</sub>
antimony triacetate	270	30	190	25
antimony triacetate	270	60	190	45
antimony triacetate	270	90	190	65
antimony triacetate	270	120	190	85
antimony triacetate	270	150	190	100
antimony triacetate	270	180	190	115
antimony triacetate	280	30	190	30
antimony triacetate	280	60	190	55
antimony triacetate	280	90	190	75
antimony triacetate	280	120	190	95
antimony triacetate	280	150	190	115
antimony triacetate	280	180	190	135
tetrabutyl titanate	280	30	20	45
tetrabutyl titanate	280	60	20	65
tetrabutyl titanate	280	90	20	85
tetrabutyl titanate	280	120	20	105
tetrabutyl titanate	280	150	20	125
tetrabutyl titanate	280	180	20	150

5

Further polycondensation reactions starting from bis-(2-hydroxyethyl)-terephthalate (BHET) were carried out in the glass equipment with screw mixer in presence of the catalysts 1 until 12.

- Catalyst of comparative example 1g : tributyltin (2-ethylhexanoate)
- 10 - Catalyst of comparative example 1h: dibutyltin bis(2-ethylhexanoate)
- Catalyst of example 1i: monobutyltin tris (2-ethylhexanoate)
- Catalyst of comparative example 1j: dibutyltin pinacolate
- Catalyst of example 1k: monooctylstannoic acid

- 24 -

- Catalyst of example 1l: monobutylstannoic acid
- Catalyst of example 1m: monooctyltin tris(2-ethylhexanoate)
- Catalyst of example 1n: monododecyltin tris(2-ethylhexanoate)
- Catalyst of example 3o: conversion product from monobutylstannoic  
5 acid with tetrabutyl titanate (4 Mol : 1 Mol)
- Catalyst of example 3p: conversion product from monooctylstannoic  
acid with tetrabutyl titanate (1 Mol : 1 Mol)
- Catalyst of example 3q: conversion product from monooctylstannoic  
acid with tetrabutyl titanate (4 Mol : 1 Mol)
- 10 - Catalyst of example 3r: conversion product from monobutylstannoic  
acid with tetrabutyl titanate (2 Mol : 1 Mol)

For the determination of the catalyst activity at first two concentrations  
of 20 ppm and 100 ppm were compared. The catalysts of (comparative)  
15 examples 1g through 1j were dissolved in toluene.

The catalysts were dissolved in dry toluene. The neat tin catalysts were  
used at a catalyst concentration of 40 ppm. The mixed catalysts  
(catalyst of examples 3o through 3q) were used at a tin content of 20  
20 ppm. For the catalyst of example 3r the tin content of the catalyst was  
22.9 ppm.

The tables 4a and 4b show the tin content and dosed catalyst amounts  
of the respective experiments.

25

BHET and the catalyst were introduced into the reaction vessel and  
rinsed well with nitrogen.

The reaction vessel was placed into the salt bath. Recording of reaction  
30 time started now. Within 15 min the pressure was lowered from 100



mbar to 0,09 mbar. At the end of the reaction a pressure of 0,04 mbar was reached.

The results are shown in the tables 5 to 15.

5

The following tables show the results of the polycondensation experiments. Criteria of the catalyst activity are the attainable molecular masses in specific time periods, the increasing influence of the thermal degradation, recognizable by the flattening of the  $P_n$ -t-function as well as the color values of the polyester. The amount of the evolved ethanal that directly correlates with the degree of thermal ester group cleavage is a further essential criterion of the catalyst suitability. The color values in the tables show the discoloration of the product, the a-values representing green/red-gradients and the b-values representing blue/yellow-gradients. Negative a-values correspond to green, negative b-values correspond to blue gradients. Blue shift is favored technologically.

10  
15

The comparative investigations for the catalytic activity of the selected tin compounds show that no noteworthy thermal decomposition is to be expected within 2 h of polycondensation time at temperatures of 280 °C. Therefore it is absolutely possible to synthesize even higher molecular weight polyethylene terephthalates by prolongation of the polycondensation time.

20  
25

All examined tin compounds proved as high-activity catalysts for the polycondensation of BHET which show significantly higher activity than stibious compounds. Their polytransesterification activity is superior to titanium alkoxides and titanium chelates. If required, they can be employed also in higher concentrations.

30

For the butyltin(2-ethylhexanoates) the activity sinks with increasing alkyl substitution. With regard to the achieved color values the monoalkyltin tricarboxylate are preferred to the di- and trialkyltin carboxylates.

Table 4a: Tin content and added catalyst amounts

catalyst of example/ comparative example	tin content [%]	amount in 50 ml stock solution [mg]	catalyst in reaction mixture for 20 ppm Sn [mg]	catalyst in reaction mixture for 100 ppm Sn [mg]
1g	27.8	182.27	1.8227	9.137
1h	22.9	221.8	2.218	11.09
1i	20.0	254.0	2.54	12.7
1j	35.1	144.7	1.447	7.24
1k	44.0			5.780
1l	56.0			4.535

10 Table 4b: Tin content and added catalyst amounts

catalyst of example/ comp. example	tin content [%]	amount of catalyst in 50 ml stock solution [mg]	amount of catalyst in the reaction mixture [mg] /[ppm] Sn
1m	17.5	580.57	5.8 / 40
1n	16.1	631.06	6.3 / 40
3o	21.0	241.9	2.4 / 20
3p	37.0	137.3	1.4 / 20
3q	37.5	155.5	1.6 / 22.9
3r	46.5	109.24	1.1 / 20

- 27 -

Table 5: Polycondensation of BHET in presence of the catalyst of comparative example 1g

time [min]	concentration Sn [ppm]	M <sub>n</sub> [g/Mol]	P <sub>i</sub>	color values using the CIE-LAB-system		
				L	a	b
15	100	3127	16	40.80	-0.34	-2.06
30	100	5953	31	36.15	-0.22	0.04
60	100	13943	72	29.68	-0.03	0.18
90	100	20281	105	30.04	0.04	0.52
120	100	23083	120	50.56	-1.65	1.36
30	20	3046	16			
60	20	5972	31	40.3	-0.64	-3.51
90	20	9933	51	32.33	-0.39	-1.47
120	20	13356	69	47.88	-0.49	-0.20

5 Table 6: Polycondensation of BHET in presence of the catalyst of comparative example 1h

time [min]	concentration Sn [ppm]	M <sub>n</sub> [g/Mol]	P <sub>n</sub>	color values using the CIE-LAB-system		
				L	a	b
16	100	3563	18	111	-2.89	-12.29
30	100	8099	42	71.9	-0.57	-1.11
60	100	18585	96	73.3	-0.48	0.17
90	100	22289	116	70.9	-0.61	1.46
120	100	27090	141	74.4	-0.71	1.94
30	20	5563	29	78.3	-1.15	-5.68
60	20	9172	47	70.3	-0.34	-1.13
90	20	13294	69	66.4	-0.30	1.07
120	20	17636	92	72.1	-0.3	0.0

Table 7: Polycondensation of BHET in presence of the catalyst of example 1i

time [min]	concentration Sn [ppm]	M <sub>n</sub> [g/Mol]	P <sub>n</sub>	color values using the CIE-LAB-system		
				L	a	b
15	100	4911	25			
30	100	10779	56	82.4	-1.85	0.83
60	100	19581	102	71.7	-1.14	3.94
90	100	25191	131	65.9	-1.32	8.52
120	100	28701	149	69.5	-1.11	7.69
30	20	6218	32			
60	20	11572	60	75.7	-0.42	-1.01
90	20	14656	76	68.8	-0.16	0.57
120	20	19130	99	83.58	-1.00	-0.29

5 Table 8: Polycondensation of BHET in presence of the catalyst of comparative example 1j

time [min]	concentration Sn [ppm]	M <sub>n</sub> [g/Mol]	P <sub>n</sub>	color values using the CIE-LAB-system		
				L	a	b
15	100	1995	10			
30	100	3238	17			
60	100	14769	77	81.4	-2.89	-0.96
90	100	20684	107	71	-1.21	4.13
120	100	24106	125	73.8	-1.52	5.4

- 29 -

Table 9. Polycondensation of BHET in presence of the catalyst of example 1k

time [min]	concentration Sn [ppm]	M <sub>n</sub> [g/Mol]	P <sub>n</sub>	color values using the CIE-LAB system		
				L	a	b
15	100	3066	16			
30	100	9071	47	70.9	-0.49	0.68
60	100	18234	95	69.3	-1.12	4.47
90	100	25817	134	82.5	-1.65	13.4
120	100	27261	142	79.2	-1.09	10.1

5 Table 10: Polycondensation of BHET in presence of the catalyst of example 1l

time [min]	concentration Sn [ppm]	M <sub>n</sub> [g/Mol]	P <sub>n</sub>	color values using the CIE-LAB system		
				L	a	b
15	100	1932	10			
30	100	7241	37	111.2	-4.7	-4.84
60	100	16217	84	74.7	-2	5.07
90	100	21936	114	70.3	-1.2	6.28
120	100	24761	129	69.9	-1.45	9.92

Table 11: Polycondensation of BHET in presence of the catalyst of example 1m

time [min]	concentration Sn [ppm]	M <sub>n</sub> [g/Mol]	P <sub>n</sub>	color values using the CIE-LAB system		
				L	a	b
15	40	2437	12			
31	40	5494	28	81.07	-1.86	-7.12
45	40	8602	44	71.80	-0.31	-0.23
60	40	11282	58	71.52	-0.40	0.40
90	40	16914	88	68.03	-0.21	2.70
120	40	20107	104	75.86	-0.83	2.51

5

Table 12. Polycondensation of BHET in presence of the catalyst of example 1n

time [min]	concentration Sn [ppm]	M <sub>n</sub> [g/Mol]	P <sub>n</sub>	color values using the CIE-LAB system		
				L	a	b
20	40	3317	17			
40	40	7051	36	75.66	-0.57	-2.49
60	40	11588	60	72.37	-0.50	-0.63
90	40	16132	84	64.23	-0.31	1.49
120	40	20633	107	69.23	-0.66	1.68
160	40	24053	125	74.12	-0.97	2.59

10

Table 13. Polycondensation of BHET in presence of the catalyst of example 3p and the catalyst of example 3q

catalyst of example	time [min]	molar ratio Ti/Sn	concentration Sn/Ti [ppm]	M <sub>n</sub> [g/mol]	P <sub>n</sub>	color values using the CIE-LAB-system		
						L	a	b
3p	20	1:1	20/9	3839	20			
3p	42	1:1	20/9	15454	80	67.15	-0.21	1.30
3p	96	1:1	20/9	25733	134	72.79	-1.03	0.61
3p	120	1:1	20/9	28454	148	68.06	-1.06	2.76
3q	15	1:4	20/2.25	1635	8			
3q	31	1:4	20/2.25	4734	24	86.69	-0.87	-4.38
3q	60	1:4	20/2.25	13499	70	70.38	-0.38	-0.31
3q	90	1:4	20/2.25	18759	97	73.54	-0.60	1.43
3q	120	1:4	20/2.25	23273	121	71.45	-0.77	1.09

Table 14. Polycondensation of BHET in presence of the catalyst of example 3r and the catalyst of example 3o

catalyst of example	time [min]	molar ratio Ti/Sn	concentration Sn/Ti [ppm]	M <sub>n</sub> [g/mol]	P <sub>n</sub>	Color values using the CIE-LAB-system		
						L	a	b
3r	20	1:2	20/4.5	1259	6			
3r	32	1:2	20/4.5	5043	26	111.81	-2.42	-4.93
3r	60	1:2	20/4.5	15788	82	78.13	-0.93	0.00
3r	90	1:2	20/4.5	19198	100	69.56	-0.83	1.88
3r	120	1:2	20/4.5	23098	120	87.40	-2.06	4.53
3r	20	1:4	20/2.25	1687	8			
3r	40	1:4	20/2.25	8181	42	71.67	-0.16	-0.64
3o	60	1:4	20/2.25	14469	75	77.63	-0.31	-0.56
3o	90	1:4	20/2.25	17388	90	82.78	-0.63	1.21
3o	120	1:4	20/2.25	24460	127	78.06	-0.74	0.77

5 Catalytic activity depending on the structure of the tin compounds



Table 15. Effective rate constants of the polycondensation of BHET in presence of tin compounds and/or tin-titanium mixed compounds

Catalyst of example/ [comparative example]	$k \cdot 10^3$ [mmol/g sec] Sn 20 ppm resp. $4 \cdot 10^{-5}$ mol/mol	$k \cdot 10^3$ [mmol/g sec] Sn 40 ppm resp. $8 \cdot 10^{-5}$ mol/mol	$k \cdot 10^3$ [mmol/g sec] Sn 100 ppm resp. $2 \cdot 10^{-4}$ mol/mol
3p	4.8		
3r	4.0		
3q	3.5		
3o	3.5		
1I	2.8	3.1	5.3
1k		3.4	4.4
1m		3.1	
1n		3.0	
[1h]	2.5		4.4
[1j]			4.2
1l			3.9
[1g]	1.7		3.6

5 Example 5: polycondensation starting with terephthalic acid and ethylene glycol

Experimental method

- 10 Polycondensation equipment 2 (15 l lab reactor of the Co. Juchheim, Germany) for the direct esterification and polycondensation of direct esterification products.

15 The equipment consisted of a stainless steel double jacket mixing tank reactor with 15 liters nominal volume and with conical bottom equipped with bottom discharge. The mixer was a double lever mixer, which fitted to the conical bottom, with speed control and torque measurement. A

- 34 -

glide ring seal with ethylene glycol formed the mixer lock as a sealing-liquid. The preheating of the mixing tank reactor was performed through a liquid circulation heating. The control of the temperature of the heat carrier was performed through a high temperature controller depending on the preset temperature in the reactor interior. At the lid of the reactor a feed hopper, gas dispersion tube, pressure gauge, thermometer (dipping tube), inspection window, light, overflow valve, reflux condenser and a Liebig condenser were installed next to the mixer. A pipe condenser and a condensate receiver were downstream to the reflux condenser, the Liebig condenser ended in a second condensate receiver. The condensate receiver had gassing/degassing valves, pressure gauge, overflow valve as well as a vacuum equipment at the lid next to the feeding means.

For the generation of the primary vacuum of approx. 20 mbar a membrane pump was used and a rotary valve vacuum pump was used up to the final vacuum. The pressure control was done by means of vacuum controller in connection with a magnetic valve in front of the sucking-nozzle of the pump. The exits of the condensate receiver were combined at the pressure point of measurement and connected through two cold traps switched in series and filled with liquid nitrogen.

By means of data printer following measuring data could be registered continuously:

- temperature at the lower inside wall in the reactor
- temperature in the melt (dipping tube in the lid)
- reflux condenser head temperature
- reactor internal pressure
- torque at the mixer shaft

Esterification, prepolycondensation and polycondensation were carried out in one experimental step.

20 mol terephthalic acid (TPA) were premixed intensely with 28 mol ethylene glycol (EG) until homogeneous. To this mixture the tin based catalysts were added. This mixture was filled into the reactor having been flushed with nitrogen before. The reactor was shut (time  $t_0$ ), a mixer rotation speed set to  $60 \text{ min}^{-1}$  and heated up to 230 to 240°C internal temperature. The temperature rise was followed by an increase of pressure up to approx. 4.5 bar. The generated water was distilled off via the reflux condenser, which was tempered at 115 °C. The head temperature in this case was kept between 170 and 190 °C.

The end of the esterification (time  $t_1$ ) was indicated by a drop of the head temperature and the internal pressure. For the catalyst dosing the esterification product was cooled to approx. 180°C for a short moment. Then primary vacuum was applied and the reactor heated up to an internal temperature of 270 to 275°C. Upon reaching the primary vacuum (approx. 20 mbar) the rotary valve vacuum pump was started. At a final pressure  $< 0.1 \text{ mbar}$  the polycondensation started (time  $t_2$ ), recognizable by the increasing torque. With high melt viscosities it was necessary to reduce the mixer rotation speed since the mixer shaft was equipped with a shear-pin with a 60 Nm upper limit to protect the shaft. At the end of the polycondensation (time  $t_3$ ) the mixer was disconnected and the evacuated vessel was flushed with nitrogen. The product was discharged from the reactor by the bottom discharge under nitrogen pressure. It was either poured onto a steel sheet to cool down in pellets, or the melt was led through a water bath, granulated and the product dried subsequently.

- 36 -

The material was dried in a vacuum oven at 130 °C for 6 h, then examined with respect to the intrinsic viscosities, and the color values were determined as described before.

- 5 The polycondensation starting out from terephthalic acid and ethylene glycol were carried out in presence of the catalysts of examples 1i, 1n, and 3p.

Test conditions and results are shown in tables 16a and 16b.

- 10 Table 16a: Test conditions and polycondensation experiment in the 15 l mixing tank reactor

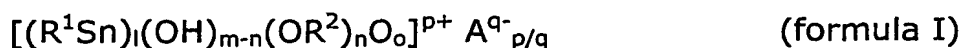
example	catalyst of example	T [°C]	concentration [ppm]	esterification time [min]	polycondensation time [min]	intrinsic viscosity
5a	1i	275	53 Sn	180	105	0.85
5b	1i	275	26.5 Sn	180	180	0.87
5c	1i	270	53 Sn	165	170	0.90
5d	1n	270	53 Sn	160	203	0.80
5e	3p	270	26.5 Sn +12 Ti	135	110	0.92

Table 16b: Results of the polycondensation experiment in the 15 l mixing tank reactor

example	M <sub>n</sub> [g/Mol]	Content of end groups x 10 <sup>6</sup> [mol/g]	Content of COOH x 10 <sup>6</sup> [mol/g]	Color value L	Color value a	Color value b	Amount of ethanal [ppm]
5a	28200	79.9	24.5	59.02	-1.19	-3.21	24
5b	29300	68.6	28	72.04	-2.08	0.28	15
5c	30700	65.1	25	70.53	-2.10	-1.20	28
5d	25600	82.3	23.5	58.14	-0.47	0.79	20
5e	31800	62.9	17	78.03	-2.62	1.17	16

## C L A I M S:

1. Catalytic composition for esterification, transesterification and  
polycondensation reactions of dicarboxylic acids, polycarboxylic acids  
and/or hydroxy carboxylic acids and alcohols containing tin compounds  
of the general formula (I):



wherein:

$R^1$  and  $R^2$  each independently is a linear, branched or cyclic alkyl group  
or aryl group having 1 to 12 carbon atoms,

$A^{q-}$  is an anion,

$l$  is at least 1,

$m = 0$  to 20,

$n = 0$  to 20,

$p = 0$  to 6,

$o = 0$  to 20 and

$q = 0$  to 6.

2. Catalytic composition according to claim 1, characterized in that  
the anion  $A^{q-}$  is  $O^{2-}$ ,  $-OH^-$ , a linear, branched or cyclic alkyl group, aryl  
carboxy group or alkoxy group each having 1 to 12 carbon atoms, the  
anion of a mineral acid or a metalate.

3. Catalytic composition according to claim 2 characterized in that  
the anion  $A^{q-}$  is a sulphate, sulphite, phosphate, halogenide or pseudo-  
halogenide, titanate, zirconate, aluminate or zincate anion.

4. Catalytic composition according to any one of claims 1 to 3 characterized in that  $n = 1$  to 20.

5 5. Catalytic composition according to anyone of claims 1 to 3 characterized in that  $l = 12$ ,  $m = 6$ ,  $n = 0$  to 6,  $o = 14$  and  $p = 2$ .

6. Catalytic composition according to anyone of claims 1 to 5 furthermore containing metal oxides, metal hydroxides and /or alkoxy  
10 metal hydroxides.

7. Process for the preparation of a catalytic composition according to any one of claims 1 to 6 wherein  $n = 1$  to 6 characterized by reacting  $[(R^1Sn)_l(OH)_mO_o]^{p+} A^{q-}_{p/q}$  with a metal alcoholate.

15

8. Process according to claim 7, characterized by using said metal alkoxide in a proportion of 1:0.0001 up to 1:20 by mole, in particular 1 : 4 to 1 : 6.

20 9. Process according to claim 7 or 8 characterized in that the resultant metal oxides, metal hydroxides and /or alkoxy metal hydroxides remain in the catalytic composition.

10. Use of the catalytic composition as defined in any one of claims 1  
25 to 9 for the continuous or batchwise production of esters or polycondensation products by esterification, transesterification, polyesterification or polytransesterification reaction.

- 40 -

11. Use according to claim 9 including a polyesterification reaction of a dicarboxylic acid derivative with a mono, divalent or polyvalent alcohol.

12. Use according to any one of claims 9 to 11, characterized by  
5 employing derivatives of di, or polycarboxylic acids being selected from the group of esters or halogenides.

13. Use according to claims 9 to 12, characterized by employing derivatives of hydroxycarboxylic acids being selected from esters.

10

14. Use according to anyone of claim 9 to 13, characterized by employing a metal concentration of said catalytic composition being in the range of 0.1 ppm to 1 mole-%, in particular 10-100 ppm with reference to the acid or derivative to be reacted.

15

15. Use according to any one of claims 9 to 14, characterized by employing a solvent or suspending agent for the manufacturing of the catalytic composition and/or said esterification, transesterification, polyesterification or polytransesterification reaction.

20

16. Use according to claim 15, characterized by employing the same solvent and/or suspending agent the manufacturing of said catalytic composition and said esterification, transesterification, polyesterification or polytransesterification reaction.

25

17. Use according to claim 15 or 16, characterized by employing a solvent or suspending agent being selected from the group of mono-, di- or polyvalent alcohols being reacted in said esterification, transesterification, polyesterification or polytransesterification reaction.

30



- 41 -

18. Polyester for bottles, films, foils, yarn and/or molded padding, or resins for powder coatings or technical synthetic materials, obtainable by a process employing a catalytic composition as defined in any one of claims 1 to 6 in a use according to any one of claims 10 to 17.

5

19. Polyester or resins according to claim 18, wherein said polyester is selected from the group of polyethylene terephthalate, poly-2,2-dimethylpropyl-1,3-terephthalate, polypropylene terephthalate, polydiethyleneglycol terephthalate, polybutylene terephthalate, polynaphthalene terephthalate, or polyethylene naphthalate.

10

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/13221

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G63/85 C08G63/82

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 114 496 A (OTERA JUNZO ET AL) 5 September 2000 (2000-09-05) claims 1-12	1-4, 10, 13-18
X	EP 0 419 254 A (ATOCHEM NORTH AMERICA) 27 March 1991 (1991-03-27)  claims 1-14	1-4, 10-12, 14-19
X	US 4 014 858 A (CHIPMAN GARY R ET AL) 29 March 1977 (1977-03-29)  column 2, line 49 - column 3, line 35	1-4, 10-12, 14-19
X	US 5 663 281 A (BRUGEL EDWARD GUS) 2 September 1997 (1997-09-02)  claims 1-9	1-4, 6, 10-12, 14-19

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

1 April 2004

Date of mailing of the international search report

13/04/2004

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Decocker, L

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/13221

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6114496	A	05-09-2000	JP 2987580 B2 JP 2000053752 A	06-12-1999 22-02-2000
EP 0419254	A	27-03-1991	US 4970288 A AT 167689 T CA 2025997 A1 DE 69032439 D1 DE 69032439 T2 EP 0419254 A2 JP 2044387 C JP 3119053 A JP 7064923 B MX 174586 B PT 95386 A ,B	13-11-1990 15-07-1998 23-03-1991 30-07-1998 19-11-1998 27-03-1991 09-04-1996 21-05-1991 12-07-1995 27-05-1994 22-05-1991
US 4014858	A	29-03-1977	BE 841664 A1 DE 2621099 A1 FR 2311051 A1 GB 1544189 A IT 1061273 B NL 7605003 A	10-11-1976 25-11-1976 10-12-1976 11-04-1979 28-02-1983 16-11-1976
US 5663281	A	02-09-1997	CA 2261293 A1 CN 1226905 A ,B EP 0915926 A1 JP 2000515924 T KR 2000029700 A WO 9804612 A1	05-02-1998 25-08-1999 19-05-1999 28-11-2000 25-05-2000 05-02-1998